Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unprecedented ferromagnetic Gd···nitronyl nitroxide coupling through hydrogen bonding bridge

Juan Sun, Meng Yang, Zan Sun, Xiufeng Wang, Yue Ma, Licun Li*

Department of Chemistry, Key Laboratory of Advancred Energy Materials Chemistry and Tianjin Key Laboratory of Metal and Molecule-based Material Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

EXPERIMENTAL SECTION

Materials and measurements

All chemicals and solvents were obtained commercially and were used in the synthesis as received without further purification. The radical ligand Nit-Ph-3,5-bIm was prepared according to the literature.[1] Elemental analyses (C, H and N) were conducted using a Perkin−Elmer 240 elemental analyzer. IR spectra were recorded in the 400–4000 cm^{-1} region using KBr pellets on a Bruker Tensor 27 Spectrophotometer. Magnetic susceptibility data were obtained from a Quantum Design SQUID VSM magnetometer using crystalline powder sample restrained in a small amount of mineral oil. Diamagnetic corrections were made for both the sample holders and the constituent atoms using Pascal's tables.[2]

Preparation of $\{[Gd(hfac)_3(Nit\text{-}Ph\text{-}3,5\text{-}bIm)(H_2O)]\cdot C_4H_{10}O\}_n$ 1

$Gd(hfac)_3\cdot 2H_2O$ (0.081g, 0.1 mmol) was added into 18 mL of hexane with refluxing for 4 hours. Then a dry solution of $CHCl_3$ (5 mL) of Nit-Ph-3,5-bIm radical (0.037g, 0.1 mmol) was added, and the resulting solution was kept at 60 °C for 15 min. The solution was then cooled to ambient temperature to afford the blue solid, which was re-crystallized from diethyl ether/hexane (2:1) to give blue crystals of **1**. Complex **1**: Yield: 56%. Anal. calc. for $C_{34}H_{26}F_{18}GdN_6O_9$ (%) (without solvent molecule

$C_2H_5OC_2H_5$): C 35.15; H 2.26; N 7.23. Found: C 35.39, H 2.41, N 7.00. IR (KBr, cm^{-1}): 3414(s), 2874(m), 1794(m), 1640(s), 1617(s), 1360(m), 1254 (s), 1160 (s), 1071 (s), 948 (s), 860 (s), 623(m), 548(s).

X-Ray Crystallography.

Structural determination of complex **1** was carried out by single-crystal X-ray diffraction. Crystallographic data were collected on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113 K. Multiscan absorption corrections were carried out using the SADABS program.[3] The structure solution was performed using SHELXS-2014 for compound **1** while the refinement was performed using SHELXL-2014 based on F^2 by the full-matrix least square technique.[4] All non-H atoms were refined anisotropic displacement parameters till convergence was reached. All the H atoms were placed at idealized positions and refined using a riding model. The crystallographic data for **1** has been deposited with the CCDC (1555610). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. Additional details of the crystallographic data and structural refinement parameters are given in Table S1. Selected bond lengths and bond angles of **1** are listed in Table S2.

Table S1. Summary of crystal data and structure refinements for **1**.

	Gd
Formula	$C_{38}H_{36}F_{18}GdN_6O_{10}$
Formula weight	1235.98
Crystal system	Orthorhombic
Space group	*Pbca*
a /Å	21.877(1)
b /Å	18.230(1)
c /Å	23.592(1)
α, deg	90
β, deg	90
γ, deg	90
V /Å^3	9445.1(9)
Z	8
D_{calcd} /g cm^{-3}	1.738
F(000)	4896
$\theta_{\mathrm{min},}$ θ_{max} deg	3.03, 27.52
Reflections collected	89398
Unique reflns/ R_{int}	10840/0.0313
GOF (F^2)	0.959
R_1/wR_2 [I> 2σ(I)]	0.0337/0.0817
$R1/wR_2$ (all data)	0.0384/0.0848

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

Bond distances			
Gd(1)-O(6)	2.401(2)	Gd(1)-O(1)	2.414(2)
Gd(1)-O(2)	2.415(2)	Gd(1)-O(3)	2.425(2)
Gd(1)-O(5)	2.454(2)	Gd(1)-O(7)	2.463(2)
Gd(1)-O(4)	2.484(2)	Gd(1)-N(3)	2.537(2)
Gd(1)-N(2)	2.586(2)	N(6)-O(9)	1.277(4)
N(5)-O(8)	1.286(4)		
Angles			
O(6)-Gd(1)-O(1)	141.39(7)	O(6)-Gd(1)-O(2)	137.78(7)
O(1)-Gd(1)-O(2)	70.03(7)	O(6)-Gd(1)-O(3)	135.64(7)
O(1)-Gd(1)-O(3)	70.82(7)	O(2)-Gd(1)-O(3)	70.10(8)
O(6)-Gd(1)-O(5)	71.88(7)	O(1)-Gd(1)-O(5)	73.00(7)
O(2)-Gd(1)-O(5)	109.28(7)	O(3)-Gd(1)-O(5)	141.40(7)
O(6)-Gd(1)-O(7)	73.46(7)	O(1)-Gd(1)-O(7)	107.81(7)
O(2)-Gd(1)-O(7)	68.53(7)	O(3)-Gd(1)-O(7)	135.90(8)
O(5)-Gd(1)-O(7)	68.81(7)	O(6)-Gd(1)-O(4)	68.17(7)
O(1)-Gd(1)-O(4)	122.81(7)	O(2)-Gd(1)-O(4)	125.87(7)
O(3)-Gd(1)-O(4)	67.70(7)	O(5)-Gd(1)-O(4)	124.84(7)
O(7)-Gd(1)-O(4)	129.37(7)	O(6)-Gd(1)-N(3)	76.41(7)
O(1)-Gd(1)-N(3)	141.57(7)	O(2)-Gd(1)-N(3)	74.24(7)
O(3)-Gd(1)-N(3)	84.25(8)	O(5)-Gd(1)-N(3)	133.82(8)
O(7)-Gd(1)-N(3)	70.54(8)	O(4)-Gd(1)-N(3)	69.33(7)
O(6)-Gd(1)-N(2)	81.12(7)	O(1)-Gd(1)-N(2)	71.28(7)
O(2)-Gd(1)-N(2)	139.94(7)	O(3)-Gd(1)-N(2)	87.80(8)
O(5)-Gd(1)-N(2)	68.06(8)	O(7)-Gd(1)-N(2)	134.85(8)
O(4)-Gd(1)-N(2)	69.55(7)	N(3)-Gd(1)-N(2)	138.06(7)

Table S3. SHAPE analysis for the Ln coordination spheres.

Compound	JCSAPR-9	CSAPR-9	JTCTPR-9	TCTPR-9
Gd	1.405	**0.237**	3.165	1.244

Table S4. Distances (Å) and angles (°) for the hydrogen bonds in compound **1**.

D–H···A	Compounds	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O7-H7B···O8	**1 Gd**	0.854(2)	1.974(2)	2.766(3)	153.7(2)

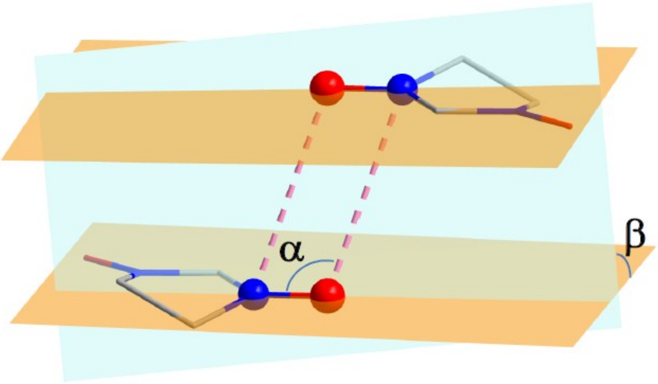

Chart S1. The relative disposition of neighboring N–O groups in **1**.

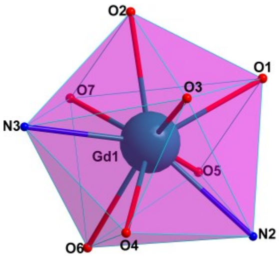

Figure S1. The core in **1**.

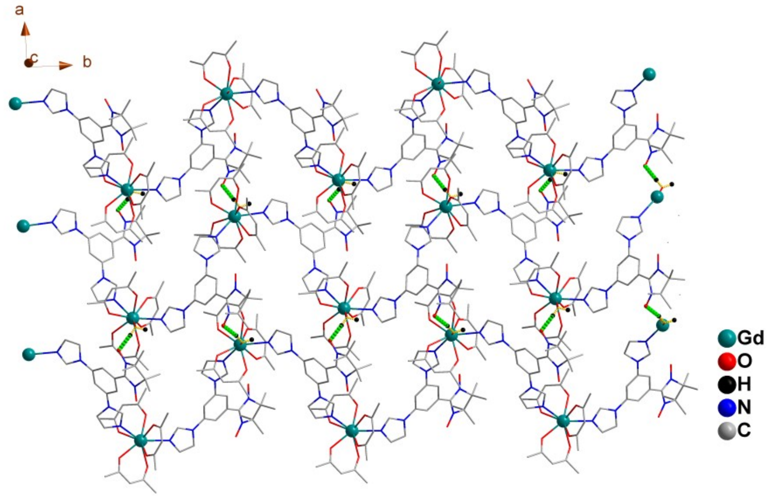

Figure S2. 2D layer structure results from the hydrogen-bonding interactions in **1**. (Diethyl ether solvent molecules, all of the F atoms and partial H atoms are omitted for clarity)

References

(1) (a) E. Maligaspe, T. Kumpulainen, H. Lemmetyinen, N, V. Tkachenko, N. K. Subbaiyan, M. E. Zandler and F. D'Souza, *J. Phys. Chem. A*, 2009, **114**, 268; (b) M. S. Davis, K. Morokuma and R. W. Kreilick, *J. Am. Chem. Soc.*, 1972, **94**, 5588.

(2) O. Kahn, Molecular Magnetism; VCH: Weinheim, **1993**.

(3) G. M. Sheldrick, *SADABS,* Program for Absorption Correction of Area Detector Frames, BRUKER AXS Inc., Madison, WI.

(4) (a) G. M. Sheldrick, SHELXS-2014, Program for structure solution, Universität of Göttingen, Germany, 2014; (b) G. M. Sheldrick, SHELXL-2014, Program for structure refinement, Universität of Göttingen, Göttingen, Germany, 2014.